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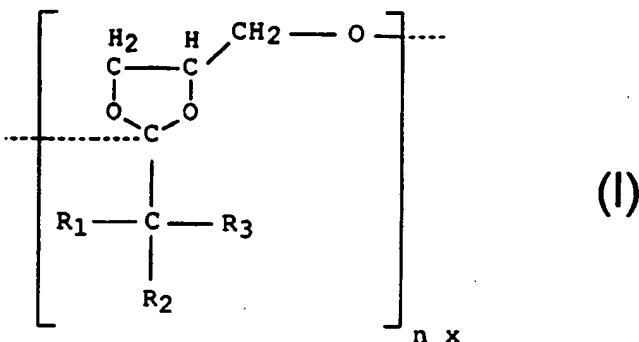
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(54) Title: ADDUCTS OF GLYCIDYLESTERS OF ALPHA, ALPHA-BRANCHED CARBOXYLIC ACIDS AND CARBOXYLIC ACIDS AND POLY(ORTHO ESTER) AS INTERMEDIATE FOR THEIR PREPARATION

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(57) Abstract: Poly(ortho ester) intermediate of general formula (I) wherein R₁, R₂ and R₃ are the same or different and each may represent an alkyl group containing from 1 to 10 carbon atoms and preferably from 1 to 6, wherein n represents an integer in the range of from 1 to 20 and preferably from 1 to 10; process for their preparation; adducts of glycidylesters and carboxylic acids and preferably acrylic acids, derived from said ortho esters; coating compositions comprising a binder component derived from said adducts.

ADDUCTS OF GLYCIDYLESTERS OF α,α -BRANCHED CARBOXYLIC ACIDS AND CARBOXYLIC ACIDS AND POLY(ORTHO ESTER) AS INTERMEDIATE FOR THEIR PREPARATION

The invention relates to adducts of glycidylesters of α,α -branched carboxylic acids and carboxylic acids, to poly(ortho ester) as intermediate for their preparation and to a process for the preparation of solid poly(ortho ester) intermediates. These adducts are useful as constituent for binders in two component curable coating compositions and more in particular curable coating compositions for clear coat or coloured top coat for automotives or general metal coatings or industrial 5 coatings.

10 Current trends in this coating market require faster curing formulations and one of the research efforts connected therewith was to change the mechanism of the oxirane ring opening, causing the formation of: fast-curing primary OH functional groups instead of the up-to-15 now occurring slow curing secondary OH group.

15 The incorporation of adducts of glycidylesters of α,α -branched carboxylic acids and e.g. acrylic acid into the (co)polymeric network obtained by radical 20 copolymerization was known from e.g. R W Tess, "Epoxy Resins, Chemistry and Technology", C A May, Ed. 2nd, Marcel Dekker 1988, p 739, R S Bauer, Chem. Tech. (1980) 692 and British Patent No. 1285520.

25 On the other hand it was known from e.g. P Citovicky, V Chrastova, J Sedlar, J Beniska and J Mejzlik, Angew. Makromol. Chem. 171(1989) 141; M Zigon, U Osredkar and A Sebenik, J. Mol. Struct., 267(1992) 123; F B Alvey, J. Polym. Sci., Part A-1, 7(1969), 2117, Q Xie, R Liao,

D Wei and J Wang, Cuihua Xuebao, 3(1982) 303, Chem. Abstr. 98: 142917; S Doslop, V Vargha and F Horkay, Period. Polytech. Chem. Eng. 22(1978) 253; H Soler, V Cadiz and A Serra, Angew. Makromol. Chem. 152(1987) 55-60 Serra, V Cadiz, P Martinez and A Mantecon, Angew. Makromol. Chem. 138(1986) 185, that the 2-OH structure was the only compound or the predominant compound formed when reacting a variety of acids with the diglycidyl-ethers and glycidylesters.

5 10 Therefore an object of the present invention was to provide modified adducts of glycidylesters of α,α -branched carboxylic acids containing in the acid moiety from 5 to 15 carbon atoms, and a carboxylic acid or an anhydride thereof, and which adducts contain predominantly primary OH groups.

15 20 Another object of the present invention was to provide a process for the preparation of said adducts in a reliable and controlled way.

Still another object of the present invention was to provide curable coating compositions which have been derived from said adducts aimed at, and show improved properties after application on in particular a metal carrier or substrate.

25 30 More in particular said object of the invention was to provide improved curable automotive top coat or clear coat compositions, comprising a copolymer derived from said adducts as one of the two components and a curing agent.

On the other hand, it was known for long that glycidylesters, when treated with Lewis acids, polymerize to form (substituted) polyethers. Whereas the older conception of using Al- and Zn-type of Lewis acids was confirmed in J C Ronda, A Serra and V Cadiz, Macromol. Chem. Phys. 200 (1999), 221, it was found by M Miyamoto,

Y Saeki, C W Lee, Y Kimura, H Maeda and K Tsutsui, *Macromolecules*, 30 (1997), 6067, that glycidyl acetate and methacrylate were converted into poly(ortho ester) when treated with methylaluminium Lewis acid. According to these authors the alternative polymerization pathway was due to the bulkiness of these specific catalysts. Therefore as the "normal" polymerization route of this present class of epoxy compounds (glycidylesters of branched acids) was regarded as the formation of polyethers and it was assumed that only in exceptional cases (strongly electron withdrawing substituent such as trifluoroacetyl or very bulky Lewis acids as catalyst) poly(ortho esters) could be formed.

As a result of extensive research and experimentation, such adducts aimed at could be surprisingly obtained.

Accordingly the invention relates to a process for the preparation of adducts of glycidylesters of α,α -branched carboxylic acids, having from 5 to 15 carbon atoms in the acid residue, and a carboxylic acid or anhydride thereof, and which adducts predominantly primary OH groups occur, comprising the oligomerization of the glycidylester into an ortho ester or poly(ortho ester), in the presence of a Lewis acid catalyst and/or a Brönsted acid (co)catalyst, and optionally in the presence of an apolar organic solvent, and subsequent conversion of said ortho ester or poly(ortho ester) with a carboxylic acid or anhydride into said adduct.

The process is preferably carried out under anhydrous conditions.

It will be appreciated that the invention also relates to the intermediate ortho esters or poly(ortho esters) and to the adducts themselves.

5 The carboxylic acids to be used for the preparation of the adduct from the intermediate ortho esters or poly(ortho esters) are preferably aliphatic or ethylenically unsaturated dicarboxylic acids, aromatic or cycloaliphatic mono-, di- or tri-carboxylic acids, or anhydrides thereof, or aliphatic branched monocarboxylic acids or ethylenically unsaturated monocarboxylic acids.

10 Suitable examples of ethylenically unsaturated mono- or di-carboxylic acids are acrylic acid, optionally substituted on the α carbon atom by an alkyl, aryl or cycloalkyl group, having from 1 to 6 carbon atoms and preferably alkyl having from 1 to 2 carbon atoms, and itaconic acid, maleic acid, fumaric acid.

15 Suitable examples of aromatic mono- or di-carboxylic acids are phthalic acid, terephthalic acid, isophthalic acid or anhydrides thereof, benzoic acid, p-tert.butyl benzoic acid, p-hydroxybenzoic acid, trimellitic acid, trimesic acid.

20 Suitable examples of aliphatic di-carboxylic acids are sebacic acid, glutaric acid, adipic acid, succinic acid, pimelic acid, $\alpha,\alpha,\alpha,\alpha$ -tetraalkylsubstituted pimelic acid, glutaric acid, adipic acid or succinic acid. Examples of cycloaliphatic carboxylic acids are hexahydrophthalic acid, hexahydrophthalic acids 25 substituted by an alkyl group having from 1 to 4 carbon atoms and preferalby 1 or 2, such as methylhexahydrophthalic acid, ethylhexahydrophthalic acid, hydrogenated trimellitic acid, 1,4-cyclohexane dicarboxylic acid, the hydrogenated Diels Alder adduct of maleic anhydride with 30 sorbic acid, or anhydrides thereof.

 Examples of suitable aliphatic monocarboxylic acids are α,α -branched aliphatic monocarboxylic acids such as VERSATIC acids having from 5 to 20 carbon atoms in the acid moiety and preferably from 8 to 12 carbon atoms.

More preferred carboxylic acid reagents are acrylic acid, methacrylic acid, VERSATIC acids having 8 to 12 carbon atoms in the acid moiety, phthalic acid, phthalic anhydride, maleic acid, maleic anhydride, adipic acid, hexahydrophthalic acid or 1,4-cyclohexane dicarboxylic acid.

5 Most preferred are acrylic acid or methacrylic acid.

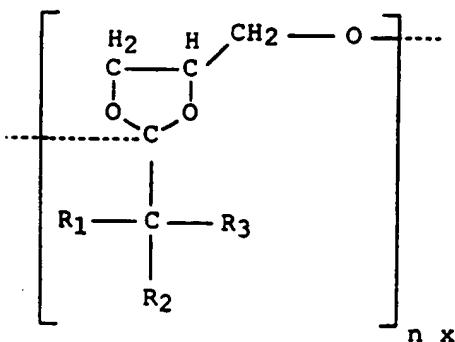
The oligomerization of the glycidylester into ortho ester or poly(ortho ester) and subsequent conversion of 10 the ortho ester with a carboxylic acid into an adduct, predominantly containing primary OH groups, are preferably carried out in a solvent selected from toluene, xylene, and trifluorotoluene (TFT) and the like.

15 The process steps are preferably carried out under anhydrous conditions.

Depending on the specific starting glycidylesters of α,α -branched carboxylic acids, the temperature must be kept under a certain maximum in order to reach as much as possible primary OH groups in said adducts.

20 In the process of the present invention the temperature is kept at at most 100 °C and more preferably at at most 80 °C and most preferably at at most 60 °C.

Accordingly the invention relates to ortho ester or poly(ortho ester) intermediate of the general formula:



wherein R₁, R₂ and R₃ are the same or different and each may represent an alkyl group containing from 1 to 10 carbon atoms and preferably from 1 to 6, wherein n represents an integer in the range of from 1 to 20 and preferably from 5 to 10.

Preferred ortho ester or poly(ortho ester) intermediates are those wherein R₁, R₂ and R₃ are methyl groups and wherein n is in the range of from 7 to 10 and those wherein the sum of the carbon atoms in R₁, R₂ and R₃ is nine and wherein R₁ represents a methyl group, and n is in the range of from 7 to 10.

Preferred intermediate ortho ester or poly(ortho esters) are prepared from glycidylesters of α,α -branched acids containing 5 or 10 carbon atoms in the acid moiety, such as the commercial products CARDURA E5 or CARDURA E10, which are glycidylesters of pivalic acid and VERSATIC acid C10 (CARDURA and VERSATIC are trademarks).

In the process for the preparation of the poly(ortho ester) intermediates as defined before, a Lewis acid catalyst can be used selected from e.g. stannous octanoate, lithium triflate, stannous triflate, scandium triflate, borontrifluoride, chromo salene, titanium tetraisopropoxide, methyltrioxorhenium, ethylaluminium 2,2'-methylenebis(6-tert.butyl-4-methylphenoxyde), methylaluminium-bis(2,5-di-tert.butyl-4-methylphenoxyde), methylaluminium-bis(2,6-di-tert.butyl-4-methylphenoxyde), chloroaluminium-bis(2,6-di-tert.butyl-4-methylphenoxyde), methylaluminium-2,2'-methylene-bis(6-tert.butyl-4-methylphenoxyde), of which scandium triflate, stannous octoate, stannous triflate, methyltrioxorhenium, boron trifluoride-ethylether, lithium triflate and titanium tetra-isopropoxide are preferred.

The Lewis acid catalyst can optionally be combined with a Brönsted acid co-catalyst, depending on the

5 specific Lewis acid catalyst type or fully replaced by such Brönsted acid. The Brönsted acids may be selected from e.g. adipic acid, maleic acid, phthalic acid, trifluoracetic acid, or trifluoromethane sulfonic acid, of which the latter being preferred.

10 A clear preferred embodiment of the process is using triflic acid as cocatalyst, forming the ortho ester intermediate at temperatures in the range from 10 to 40 °C, within an acceptable time period.

15 It will be appreciated that the reactivity of the poly(ortho ester) is different from the original starting glycidylester and that it reacts with the selected carboxylic acid to give an adduct with a predominant proportion a primary hydroxyl group and is stable in the presence of base.

20 Moreover, depending on the present type of catalyst the poly(ortho ester) can be decomposed by water. Therefore their preparation has preferably to be carried out under anhydrous conditions.

25 Accordingly another aspect of the present invention is formed by adducts of glycidylesters of α,α -branched carboxylic acids, having from 5 to 15 carbon atoms in the acid residue, and a carboxylic acid, as specified hereinbefore, said adducts predominantly containing primary OH groups, and obtainable by reaction of ortho ester or poly(ortho ester) as specified hereinbefore, with a carboxylic acid, or anhydride thereof at a temperature of below a critical value dependent on the specific type of the starting glycidylester but in general below 100 °C and preferably below 90 °C. More in particular temperatures are in the range of from 90 to 40 °C and preferably from 50 to 70 °C.

30 For example the maximum temperature is 60 °C if the ortho ester has been derived from CARDURA E5

glycidylester and 90 °C if the ortho ester has been derived from CARDURA E10 glycidylester.

With the term "predominantly containing primary OH groups" as used throughout the present specification is meant that 50% or more of the total OH groups formed during the reaction of the poly(ortho ester) intermediate and an carboxylic acid and preferably acrylic acid, will be primary OH groups.

Preferably the fraction of primary OH groups will be at least 60%, and more preferably at least 80%.

More preferred are adducts, wherein the fraction of primary OH groups formed is at least 70% of the total number formed and preferably at least 80% of the total number formed.

It will be appreciated that another aspect of the present invention is formed by a process for the straight preparation of adducts, predominantly containing primary OH groups, via conversion of an ortho ester or a poly(ortho ester) as specified hereinbefore with a carboxylic acid or anhydride thereof, without any isolation of said poly(ortho ester) at a temperature in the range of from 40 to 100 °C.

Another aspect of the present invention is formed by coating compositions, comprising at least a binder component and a liquid carrier, wherein the binder is a copolymer derived from one or more hereinbefore specified adducts as constituents, and optionally one or more additional comonomers having ethylenic unsaturation, by copolymerization by means of a radical initiator, and a cross-linker and a curing catalyst.

The binder copolymers used for coating compositions and in particular automotive coating compositions, have usually a total OH content (% m/m) in the range of from 3.10 to 3.25, a Mw in the range of from 3900 to 4200 and

Mw/Mn ratio in the range of from 1.4 to 1.8 and preferably from 1.5 to 1.7.

The viscosity (in mPa.s) of the copolymer solution at 60 wt% solids is usually in the range of from 180 to 320 at 22.5 °C. For example the maximum temperature is 60 °C if the ortho ester has been derived from CARDURA 5 esters and 95 °C if ortho ester has been derived from CARDURA 10.

Preferably these coating compositions comprise in addition a component, which is formed by a hydroxy-functional oligoether, derived from at least one polyol, free of carboxyl groups and having three or four hydroxyl groups and a monoglycidylester of an α,α -branched carboxylic acid containing from 5 to 15 carbon atoms.

More preferably said additional hydroxyfunctional oligoether applied, has a number average molecular weight Mn of from 150 to 1000, a molecular weight distribution MWD < 1.8 and a hydroxy value of between 180 and 700.

The coating compositions according to the present invention usually may contain one or more cross-linkers.

Many examples of such cross-linkers are commercially available as will be appreciated by those skilled in the coatings art. A preferred class of cross-linkers is formed by the polyisocyanate cross-linkers.

Various isocyanates employed as cross-linking agents are described in U.S. patent No. 4,322,508. However, the biuret or cyclotrimer of hexamethylene diisocyanate or isophorone diisocyanate are preferred.

Trifunctional isocyanates may be used, for example, triphenylmethane triisocyanate, 1,3,5-benzene tri-isocyanate, 2,4,6-toluene triisocyanate, an adduct of trimethylol and tetramethyl xylene diisocyanate sold under the trade name "Cythane 3160," "DESMODUR" N 3390 which is the timer of hexamethylene diisocyanate, and the

like (DESMODUR is a trademark). Optionally, one can use a polyisocyanate acrylic copolymer derived from isocyanatoethyl methacrylate (commercially available as TMI) and the like, as, for example, disclosed in 5 U.S. patent 4,965,317 (col. 5).

As most preferred polyisocyanate cross-linker is used the cyclotrimer of hexamethylene diisocyanate.

Other film forming polymers, preferably in an amount of from 0 to 10 wt%, relative to the weight of the 10 binder, may also be used in conjunction with the above-mentioned components. Other film-forming polymers may be linear or branched and may include acrylics, acrylo-urethanes, polyesters, polyester urethane, polyethers, and polyether urethanes that are compatible with the 15 other components of the binder.

In addition, a coating composition according to the present invention may contain a variety of other optional 20 ingredients, including pigments, pearlescent flakes, fillers, plasticizers, antioxidants, surfactants and flow control agents.

To improve weatherability of a finish produced by the present coating composition, an ultraviolet light 25 stabilizer or a combination of ultraviolet light stabilizers can be added in the amount of about 0.1-3% by weight, based on the weight of the binder. Such stabilizers include ultraviolet light absorbers, screeners, quenchers, and specific hindered amine light stabilizers. Also, an antioxidant can be added, in the 30 about 0.1-3% by weight, based on the weight of the binder.

Typical ultraviolet light stabilizers that are useful include benzophenones, triazoles, triazines, benzoates, hindered amines and mixtures thereof. Specific examples

of ultraviolet stabilizers are disclosed in U.S. patent No. 4,591,533.

5 The composition may also include conventional formulation additives such as flow control agents, for example, RESIFLOW S (polybutylacrylate) (RESIFLOW is a trademark), BYK 320 and 325 (high molecular weight polyacrylates) (BYK is a trademark); rheology control agents, such as fumed silica, microgels, and non-aqueous dispersion polymers; water scavengers such as 10 tetrasilicate, trimethyl orthoformate, triethyl orthoformate, and the like.

15 When the present composition is used as a clearcoat (topcoat) over a pigmented colourcoat (basecoat) to provide a colourcoat/clearcoat finish, small amounts of pigment can be added to the clear coat to provide special colour or aesthetic effects such as tinting.

20 The present composition can be pigmented and used as the colourcoat, monocoat, primer, or primer surfacer. The composition has excellent adhesion to a variety of metallic or non-metallic substrates, such as previously 25 painted substrates, cold rolled steel, phosphatized steel, and steel coated with conventional primers by electrodeposition. The present composition can also be used to coat plastic substrates such as polyester reinforced fibreglass, reaction injection-moulded urethanes and partially crystalline polyamides.

30 When the present coating composition is used as a basecoat, typical pigments that can be added to the composition include the following: metallic oxides such as titanium dioxide, zinc oxide, iron oxides of various colours, carbon black, filler pigments such as talc, china clay, barytes, carbonates, silicates and a wide variety of organic coloured pigments such as quinacridones, copper phthalocyanines, perylenes, azo

5 pigments, indanthrone blues, carbazoles such as carbazole
 violet, isoindolinones, isoindolones, thioindigo reds,
 benzimidazolinones, metallic flake pigments such as
 aluminum flake and the like.

10 5 The pigments can be introduced into the coating
 composition by first forming a mill base or pigment
 dispersion with any of the afore-mentioned polymers used
 in the coating composition or with another compatible
 polymer or dispersant by conventional techniques, such as
 high speed mixing, sand grinding, ball milling, attritor
 grinding or two roll milling. The mill base is then
 blended with other constituents used in the coating
 composition to obtain the present coating compositions.

15 10 The coating composition can be applied by
 conventional techniques such as spraying, electrostatic
 spraying, dipping, brushing, flowcoating and the like.
 The preferred technique is spraying.

20 15 It will be appreciated that another aspect of the
 present invention is formed by cured coating composition
 layers on a carrier or support, the coating compositions
 comprising as binder a copolymer, wherein an adduct as
 defined hereinbefore is one of the constituents.

25 20 The present invention is illustrated by the following
 examples, however, without restricting its scope to these
 embodiments.

Example 1

30 25 At room temperature 5.0 g of CARDURA E5 glycidylester
 (32 mmol) and the selected catalyst (e.g. 121.5 mg
 stannous octoate) were intimately mixed and heated at the
 temperature listed in table 1, while stirring
 magnetically.

 At specified intervals samples were drawn cooled to
 room temperature dissolved in CDCl₃, and analysed by ¹H-
 NMR and ¹³C NMR spectroscopy. In some cases stirring

became impossible at high conversions of glycidyl pivalate, because of the increased viscosity.

When the general procedure was run at 60 °C for 5 days, all glycidyl pivalate had been converted (no residual epoxy groups detectable by NMR). The crude mixture was dissolved in chloroform and subjected to VPO-analysis (Vapour Phase Osmometry). The average number molecular weight was found to be 1263, indicating a degree of polymerisation of 8.7. The same sample was also subjected to SEC (Size Exclusion Chromatography) and showed an average number molecular weight of 1153 (EPIKOTE reference scale) and a molecular weight distribution $M_w/M_n = 1.62$.

The reaction mixtures derived from glycidyl pivalate 15 were analysed by means of $^1\text{H-NMR}$. The reaction products of CARDURA E5 consist of polyether (PE), poly(ortho ester) (POE), and the glycerol orthopivalate (OE). Each of the components exhibit very characteristic absorptions in the $^1\text{H-NMR}$ spectrum in CDCl_3 allowing the quantitative 20 determination of the product composition.

The starting glycidyl pivalate showed characteristic peaks at 2.66, 2.86 and 3.22 ppm for the three protons in the vicinity of the epoxy group respectively.

The characteristic polyether (PE) proton was observed 25 as a rather broad absorption at 5.1 ppm. The presence of a monomeric ortho ester (OE) was most clearly revealed by its ter.butyl absorption at 1.18 ppm or alternatively by the characteristic proton connected to the common carbon atom of the three monomeric orthopolyester rings, at 30 4.93 ppm. The poly(ortho ester) (POE) was characterized by its unique tert.butyl absorption at 1.00 ppm.

Table 1

Reaction of near CARDURA E5 glycidylester catalysed by
 SnOct_2 (1 mol %)

temp (°C)	time (h)	product (yield, %) ^a			GPC ^b	
		OE	POE	PE	Mn	Mw
60	24	0	56	tr		
60	120	0	99	tr	1153	1868
80	24	0	83	tr		
80 ^c	96	0	93	tr		
80	72	tr	92	tr	1404	2130
80	96	tr	92	tr		
80 ^d	144	0	98	tr		
100	25	tr	96	tr	871	1284
100	24	tr	95	tr		
100	48	tr	93	tr		
100	48	tr	100	tr		
120	24	tr	72	20	1159	1743
140	24	tr	60	40	1097	1529
	48	0	49	51		
	120	0	27	73		

a. tr=trace amounts; b. Epikote reference scale;

c. 0.01 mol% acrylic acid present; d. 1 mol% acrylic acid present.

The influence of solvents on the catalysed POE-formation is illustrated in Table 2.

Table 2
**Solvent effect on SnOct_2 (1% molar) catalysed
 POE-formation from CARDURA E5 glycidylester**

solvent	temp (°C)	time (h)	product (yield, %) ^a		
			OE	POE	PE
none	80	24	0	76	tr
		72	0	91	tr
toluene ^b	100	68	tr	25	tr
THF	65	24	8	25	tr
		72	tr	44	20
TFT	100	24	4	43	4
		72	7	53	10

a. tr=trace amounts; b. 30 mmol (5 g) Cardura in 10 g solvent.

The influence of different Lewis acids towards CARDURA E5 glycidylester and the reaction of neat CARDURA E5 glycidylester catalysed by various Lewis acids have been illustrated in Tables 3 and 4.

Table 3
 Reactivity of different Lewis acids towards CARDURA ES
 glycidylester

catalyst	moles (%)	temp (°C)	time (h)	CARDURA glycidyl- ester conversion (%)
Sc(tf) ₃	0.1	25	1	32
Bf ₃ .OEt ₂	0.1	25	1	30
Sn(tf) ₂	0.1	25	20	26
Sn(tf) ₂	1	25	2	53
Sc(tf) ₃	1	100	1	100
Cr-salene	1	100	2	78
SnOct ₂	1	100	2	64
Ti(OiPr) ₄	1	100	2	33
MTO	1	100	2	21
Sn(OAc) ₂	2	100	24	95
SnOct ₂	2	100	24	89
Sc(OAc) ₃	2	100	24	70
Zn(OAc) ₂	2	100	24	45
Li(tf)	2	100	24	23

Table 4
 Reaction of neat CARDURA E5 glycidylester catalysed by
 various Lewis acids

catalyst	moles (%)	temp (°C)	time (h)	product(yield, %) a			GPC ^b	
				OE	POE	PE	Mn	Mw
SnOct ₂	1	100	25	tr	96	tr	871	1284
SnOct ₂	0.8	100	4	5	80	15		
SnOct ₂	0.1	120	24	tr	67	33	1159	1743
Sn(tf) ₂	1	25	20	6	81	7	366	462
Sc(tf) ₃	0.13	25	1	26	61	tr	358	728
Sc(tf) ₃	0.07	25	8	9	59	5		
Sc(tf) ₃	0.1	25	20	8	56	26		
Li(tf)	2	100	72	tr	100	0	2368	4316
TMStf	1	25	24	10	60	18		
BF ₃ .OEt ₂	0.25	25	20	20	73	tr	365	421
BF ₃ .OEt ₂	0.1	25	20	6	70	16	554	665
BF ₃ .OEt ₂	1	25	1	9	70	8	1159	1743
Ti(OiPr) ₄	1	100	24	tr	84	tr	1205	2284
MTO	1	100	24	6	59	20		
Cr-salene	1	100	2	56	22	tr		
Sc(oAc) ₃	2	100	24	55	10	5		

Sc(tf)₃ = scandium triflate

BF₃.OEt₂ = boron trifluoride-diethylether

Sn(tf)₂ = stannous triflate

Sn(tf)₃ = stanni triflate

Cr-salene = chromic salene

SnOct₂ = stannous octoate

Sc(oAc)₃ = scandium acetate

Ti(OiPr)₄ = titanium isopropoxide

MTO = methyl trioxorhenium

$\text{Sn}(\text{oAc})_2$ = stannous acetate
 $\text{Sn}(\text{oAc})_3$ = stanni acetate
 $\text{Zn}(\text{oAc})_2$ = zinc acetate
 $\text{Li}(\text{tf})$ = lithium triflate
TMStf = trimethylsilyl trifluoromethanesulfonate
(B[DBMP]MA) = bis(2,5-di-tert.butyl-4-methylphenoxide)
methyl aluminium

The Lewis acid catalysed reaction of CARDURA E5 in different solvents and the catalytic effect of Brönsted acids is illustrated in Tables 5 and 6.

Table 5
Lewis acid catalysed reaction of CARDURA E5 glycidylester in different solvents

solvent (conc)	catalyst (g m)	temp (°C)	time (h)	product(yield, %) a			GPCD Mn	MW
				OE	POE	PE		
none	BF ₃ .OEt ₂ (0.25)	25	20	20	73	tr	365	421
toluene	BF ₃ .OEt ₂ (1.5M) (1%)	25	24	29	71	tr		
none	Sc(tf)3 (0.13%)	25	1	26	61	tr	358	728
toluene	Sc(tf)3 (5.2M) (0.13%)	25	0.25	5	95	tr		
none	Sc(tf)3 (0.07%)	25	8	9	59	5		
TFT	Sc(tf)3 (2.5M) (0.07%)	25	1	11	78	tr		
none	B[DBMP]MA (0.3%)	100	24	48	37	tr		
toluene	B[DBMP]MA (1.4M) (4%)	25	0.25	tr	100	tr	6280	19440

a. tr=trace amounts; b. Epikote reference scale

Table 6
 Brönsted acids catalysed reaction of CARDURA E5
 glycidylester

catalyst	moles (%)	temp (°C)	time (h)	product (yield, %) ^a		
				OE	POE	PE
acrylic acid	5	60	120	0	0	0
CF ₃ CO ₂ H	6	25	96	tr	6	tr
CF ₃ SO ₃ H	0.2	60	1	tr	54	30
CF ₃ SO ₃ H	1	25	18	18	55	18
CF ₃ SO ₃ H	0.5	25	4.5	25	50	10
			22	15	60	20

a. tr=trace amounts

The catalyst bis(2,5-ditert.butyl-4-methyl-phenoxide)methyl aluminium (B[DBMP]MA) used in Tables 5 and 6 was prepared by addition in portions of 1.10 g (5 mmol) of ditert.butyl-4-methylphenol to 1.25 ml of a 5 2M solution of trimethyl aluminium in toluene (2.5 mmol). The clear mixture was stirred for 20 hours at room temperature. Evaporation of the solvent gave B[DBMP]MA in almost quantitative yield and showing the following characteristics ¹H NMR (CDCl₃): 7.245 (s, 4H), 2.371 (s, 6H), 1.654 (s, 36H), -0.2 (s, 3H).

Example 2

Poly(ortho esters) of CARDURA E10 glycidylester were prepared under the conditions listed in Table 7.

Table 7

Reaction of neat CARDURA E10 glycidylester catalysed by various Lewis acids

catalyst	moles (%)	temp (°C)	time (h)	product (yield, %) ^a			GPC ^b	
				OE	POE	PE	Mn	Mw
SnOct ₂	1	60	72	tr	26	tr		
SnOct ₂	1	80	72	tr	34	51		
SnOct ₂	1	100	48	0	26	51		
Sn(tf) ₂	1	25	24	tr	71	20		
Sc(tf) ₃	0.067	25	72	0	major	minor	508	573
Litf	2	100	72	tr	55	35		

Example 3(a)

The reactivity of the poly(ortho ester) of CARDURA E5 glycidylester with several selected reagents was tested in toluene, as depicted in Table 8.

Table 8

Reaction of the poly(ortho ester) of CARDURA E5 with some selected reagents in toluene^a

catalyst used in prepar- ation	reagent (molar ratio)	temp. (°C)	time (h)	conversion (%)	product
SnOct ₂	acrylic acid (1)	60	20	93	18% 1-OH 75% 2-OH
SnOct ₂	acrylic acid (2)	100	0.4	100	53% 1-OH 47% 2-OH
SnOct ₂	acrylic acid (2)	100	0.75	87	47% 1-OH 40% 2-OH

Table 8 (cont'd)

catalyst used in preparation	reagent (molar ratio)	temp. (°C)	time (h)	conversion (%)	product
SnOct ₂	benzoic acid (1)	100	0.17	86	85% 1-OH 15% 2-OH
SnOct ₂	cyclo-hexane carboxylic acid (1)		0.40	85	75% 1-OH 25% 2-PH
Litf	acrylic acid (2)	100	0.25 1.5	100 100	>90% 1-OH 30% 1-OH 70% 2-OH
B[DBMP]MA	acrylic acid (0.6)	100	0.5	70	53% 1-OH 17% 2-OH
SnOct ₂	p-tert.-butyl benzoic acid (2)	100	0.75	93	40% 1-OH 53% 2-OH
SnOct ₂	H ₂ O (2)	100	1	0	
SnOct ₂	H ₂ O (9)	100	84	100	glycerol pivalate
	CH ₃ CN/H ₂ O	25	20 175	0 82	glycerol pivalate (40% 1-, 60% 2- substituted)

Table 8 (cont'd)

catalyst used in preparation	reagent (molar ratio)	temp. (°C)	time (h)	conversion (%)	product
	standing in air ^b	25	100	100	glycerol pivalate (17% 1-, 83% 2-substituted)
	D ₂ O ^b	25	150	<30	
CF ₃ SO ₃ H	H ₂ O ^b	25	96	100	mainly PE no glycerol pivalate
CF ₃ SO ₃ H	standing in air ^b	25	1	100	>90% 1-substituted
SnOct ₂	MeOH ^d	25	168	100	*
catalyst used in preparation	reagent (molar ratio)	temp. (°C)	time (h)	conversion (%)	product
SnOct ₂	aniline (2)	100	3	0	

a. concentration about 1.0-1.5M; b. no solvent; c. no residual OE, 30% residual POE; d. about 1M solution in methanol

* poly(ortho ester) of CARDURA E5 glycidylester formed monocyclic ortho ester, if dissolved in methanol; evaporation of the solvent led to the poly(ortho ester) again.

Example 3b

5 Adduct of acrylic acid and of CARDURA E10 glycidylester (ACE; 85 mole% 1-O H isomer) was prepared (via the intermediate ortho ester) from a mixture of 24.6 g (100 mmol) of CARDURA E10 glycidylester, 100 ml of toluene, 7.92 g (110 mmol) of acrylic acid and 0.61 g (1.5 mmol) of Sn-octanoate. Said mixture was heated to 110 °C. After 5 hours the reaction mixture was evaporated. The yield was 30 g of ACE-adduct (100%, 10 purity 86.5 by GC analysis and $^1\text{HNMR}$. Said product (I) consisted of 85 mole% adduct isomer, containing a primary hydroxy group (1-OH isomer) and 15 mole% adduct isomer, containing a secondary hydroxy group (2-OH isomer).

15 Adduct of acrylic acid and CARDURA E10 glycidylester ACE (80 mole% 2-OH) was prepared by refluxing a solution of 505 mmol CARDURA E10 glycidylester, 500 mmol acrylic acid, 15 mmol EtPPI, 50 ppm (3.5 mg) of 4-ethoxyphenol and 400 ml of ter.-amyl-methylether at 80 °C during 24 hours, giving a yield of about 85%. After treatment of 20 the cooled solution with 10 eg. AMBERLITE ion exchanger during 45 minutes at room temperature filtration, again treatment of the solution with AMBERLITE during 1 hour at room temperature, filtration and vacuum evaporation at room temperature, the 2-OH isomer was isolated in almost 25 quantitative yield (product II) with a content of 2-OH isomer of 80 mol% and 1-OH isomer of 20 mole%.

30 The preformed ACE-adducts were copolymerized with other acrylic monomers to form an OH functional acrylic polymer resins I and II.

35 Into a round-bottomed glass reactor equipped with a stainless steel anchor stirrer, thermocouple and reflux condensor, the solvent was charged and heated until 140 °C. When the solvent reached said temperature, a mixture of the specific ACE adduct with the other comonomers and the initiator was added over a period of

4 hours followed by a post reaction of 2 hours with a supplement of initiator. The respective comonomer proportions and other details have been listed in the Table 9.

Table 9

	ingredients in parts weight
Initial reactor charge:	
Xylene	25
Monomer feed:	
ACE adduct I or II	58.5
Butylacrylate	6.5
Styrene	30
Methylmethacrylate	5
Di-tert.amylperoxide	4
Post-addition:	
Di-tert.amylperoxide	1

5 The resins obtained were evaluated by their final acid value, weight average molecular weight (Mw), molecular weight distribution (Mwd) and solids content.

10 The resins were first further diluted until 80% solids content with xylene and thereafter with butylacetate until 60% solids content to obtain the same solvent ratios.

At 60% solids content the coloud and viscosity was measured.

Table 10

	adduct resin I	adduct resin II
Polymer properties:		
Total OH content (%m/m)	3.18	3.18
Mw	4995	4156
Mw/Mn	1.7	1.54
Solution properties		
(at 60% solids):		
Viscosity (mPa.s)	309 at 22.4 °C	224 at 23.2 °C
Solids content (%w)	59.9	60.4
Colour (Pt/Co)	137.4	<20

Curing of resins

In order to evaluate the reactivity of the resins, blends with isocyanate curing agents and a cure catalyst were prepared. After application, the conversion was followed by decrease in isocyanate concentration as well as hardness development of the surface.

5

Details have been listed in Table 11.

Table 11

c) Copolymer resin of an adduct OH-1 (adduct resin I)				curing of the copolymer resin of adduct OH-1 adduct resin I			
Time (hours)	Koenig hardness, heat cured	Time (hours)	Koenig hardness, ambient cured	Time (hours)	NCO (relative absorbance)	Time (hours)	NCO (relative absorbance)
0.5	3	0.5	0	1	5.21		
1	4	1	0	2.33	4.16		
27	39	27	23	3	3.81		
41.5	70	41.5	51	20.25	0.63		
68.5	109	68.5	90	25.9	0.41		
89.5	133	89.5	110	55.6	0.05		
162.5	167	163	144				

e) Copolymer resin of an adduct OH-2 (adduct resin II)				curing of the copolymer resin of adduct OH-2 adduct resin II			
Time (hours)	Koenig hardness, heat cured	Time (hours)	Koenig hardness, ambient cured	Time (hours)	NCO (relative absorbance)	Time (hours)	NCO (relative absorbance)
0	0	0	0	1	5.20		
1.5	0	2	0	2.33	4.36		
20	14	20.5	10	3	4.10		
26	17	26.75	15	20.25	1.90		
68	51	140.5	63	25.9	1.60		
141	72			55.6	0.60		

Example 4

Adducts containing predominantly primary OH groups, of maleic acid or adipic acid, and of CARDURA E10 glycidylester, were prepared (via the intermediate ortho ester or poly(ortho ester) from a mixture 24.6 g (100 mmol) of CARDURA E10 glycidylester, 100 ml of toluene, 110 mmol of maleic acid or adipic acid (12.8 g and 16.2 g respectively), and 0.61 g (1.5 mmol) of Sn-octanoate or without any catalyst at all.

Said mixtures were heated to a temperature in the range of from 90 to 110 °C. The results and relevant reaction conditions have been listed in Table 12. After the indicated time periods, the reaction mixture was evaporated and the yield of the adduct, aimed at, was estimated via GC analysis and ^1H NMR.

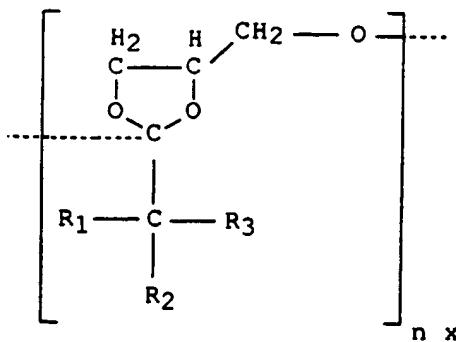
Table 12

Exp.	temp.	time	catalyst	prim. OH %
1	110 °C	30 m CE + maleic acid	SnOct	69.30
2	110 °C	30 m CE + adipic acid	SnOct	77.03
3	110 °C	1 hr CE + adipic acid	SnOct	81.34
4	110 °C	30 m CE + adipic acid	none	86.84
5	109 °C	3 h CE + adipic acid	none	83.17
6	110 °C	5 h CE + adipic acid	none	72.70
7	90 °C	30 m CE + maleic acid	SnOct	78.89
8	90 °C	90 m CE + maleic acid	SnOct	77.24

CE = CARDURA E10 glycidylester.

C L A I M S

1. Ortho ester or poly(ortho ester) intermediate of the general formula:

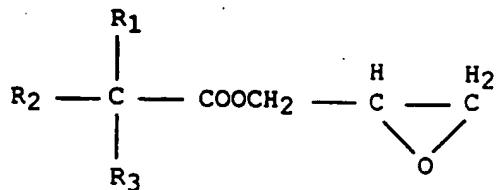


wherein R₁, R₂ and R₃ are the same or different and each may represent an alkyl group containing from 1 to 5 carbon atoms and preferably from 1 to 6, wherein n represents an integer in the range of from 1 to 20 and preferably from 1 to 10.

5 2. Ortho ester or poly(ortho ester) intermediate according to claim 1, wherein R₁, R₂ and R₃ are methyl groups and wherein n is in the range of from 1 to 10.

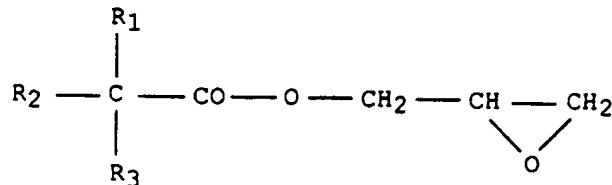
10 3. Ortho ester or poly(ortho ester) intermediate according to claim 1, wherein the sum of the carbon atoms in R₁, R₂ and R₃ is nine and wherein R₁ represents a methyl group, and n is in the range of from 7 to 10.

15 4. Ortho ester or poly(ortho ester) intermediate according to claim 1, obtainable by polymerization of glycidylesters of the formula:



wherein R₁, R₂ and R₃ are as defined hereinbefore, in the presence of at least a Lewis acid catalyst and/or Brönsted acid cocatalyst and optionally in the presence of an apolar organic solvent.

5 5. Process for the preparation of poly(ortho ester) intermediate according to claims 1-4, comprising the oligomerization of the glycidylester of an α,α -branched acid of the formula:



10 in the presence of a Lewis acid as catalyst and/or a Brönsted acid as cocatalyst and optionally in the presence of an apolar solvent at a temperature of at most 110 °C.

15 6. Process according to claim 5, characterized in that anhydrous conditions are used.

7. Process according to claim 5, characterized in that Sn octanoate is used as Lewis acid.

8. Process according to claim 5, characterized in that Sn triflate is used as Lewis acid at a temperature lower than 60 °C.

20 9. Process according to claim 5, characterized in that Li-triflate is used as Lewis acid at a temperature lower than 60 °C.

10. Process according to claim 5, characterized in that triflic acid is used as Brönsted acid catalyst at a polymerization temperature lower than 60 °C.

25 11. Adducts of glycidylesters of α,α -branched carboxylic acids, having from 5 to 15 carbon atoms in the acid residue, and a carboxylic acid or anhydride thereof, said adducts predominantly containing primary OH groups, and obtainable by reaction of poly(ortho ester) according to

claims 1-4, with a carboxylic acid, at a temperature of at most 110 °C and preferably at most 80 °C and more preferably in the range of from 50 to 70 °C.

5 12. Adducts of glycidylesters of α,α -branched carboxylic acids having 5 carbon atoms in the acid residue, and an aromatic carboxylic acid, ethylenically unsaturated carboxylic acid, a (cyclo)aliphatic carboxylic acid and preferably an acrylic acid optionally substituted on the α C-atom by an alkyl of from 1 to 4 carbon atoms, said adducts predominantly containing primary OH groups, and obtainable by reaction of an ortho ester or a poly(ortho ester) according to claim 2, with said carboxylic acid or an anhydride thereof, at a temperature of at most 60 °C.

10 13. Adducts of glycidylesters of α,α -branched carboxylic acids having 10 carbon atoms in the acid residue, and an aromatic carboxylic acid, ethylenically unsaturated carboxylic acid, a (cyclo)aliphatic carboxylic acid and preferably an acrylic acid optionally substituted on the α C-atom by an alkyl of from 1 to 4 carbon atoms, said adducts predominantly containing primary OH groups, and obtainable by reaction of an ortho ester or a poly(ortho ester) according to claim 2, with an optionally substituted acrylic acid at a temperature of at most 100 °C.

15 20 25 30 35 40 45 50 55 60 65 70 75 80 85 90 95 100 105 110 115 120 125 130 135 140 145 150 155 160 165 170 175 180 185 190 195 200 205 210 215 220 225 230 235 240 245 250 255 260 265 270 275 280 285 290 295 300 305 310 315 320 325 330 335 340 345 350 355 360 365 370 375 380 385 390 395 400 405 410 415 420 425 430 435 440 445 450 455 460 465 470 475 480 485 490 495 500 505 510 515 520 525 530 535 540 545 550 555 560 565 570 575 580 585 590 595 600 605 610 615 620 625 630 635 640 645 650 655 660 665 670 675 680 685 690 695 700 705 710 715 720 725 730 735 740 745 750 755 760 765 770 775 780 785 790 795 800 805 810 815 820 825 830 835 840 845 850 855 860 865 870 875 880 885 890 895 900 905 910 915 920 925 930 935 940 945 950 955 960 965 970 975 980 985 990 995 1000 1005 1010 1015 1020 1025 1030 1035 1040 1045 1050 1055 1060 1065 1070 1075 1080 1085 1090 1095 1100 1105 1110 1115 1120 1125 1130 1135 1140 1145 1150 1155 1160 1165 1170 1175 1180 1185 1190 1195 1200 1205 1210 1215 1220 1225 1230 1235 1240 1245 1250 1255 1260 1265 1270 1275 1280 1285 1290 1295 1300 1305 1310 1315 1320 1325 1330 1335 1340 1345 1350 1355 1360 1365 1370 1375 1380 1385 1390 1395 1400 1405 1410 1415 1420 1425 1430 1435 1440 1445 1450 1455 1460 1465 1470 1475 1480 1485 1490 1495 1500 1505 1510 1515 1520 1525 1530 1535 1540 1545 1550 1555 1560 1565 1570 1575 1580 1585 1590 1595 1600 1605 1610 1615 1620 1625 1630 1635 1640 1645 1650 1655 1660 1665 1670 1675 1680 1685 1690 1695 1700 1705 1710 1715 1720 1725 1730 1735 1740 1745 1750 1755 1760 1765 1770 1775 1780 1785 1790 1795 1800 1805 1810 1815 1820 1825 1830 1835 1840 1845 1850 1855 1860 1865 1870 1875 1880 1885 1890 1895 1900 1905 1910 1915 1920 1925 1930 1935 1940 1945 1950 1955 1960 1965 1970 1975 1980 1985 1990 1995 2000 2005 2010 2015 2020 2025 2030 2035 2040 2045 2050 2055 2060 2065 2070 2075 2080 2085 2090 2095 2100 2105 2110 2115 2120 2125 2130 2135 2140 2145 2150 2155 2160 2165 2170 2175 2180 2185 2190 2195 2200 2205 2210 2215 2220 2225 2230 2235 2240 2245 2250 2255 2260 2265 2270 2275 2280 2285 2290 2295 2300 2305 2310 2315 2320 2325 2330 2335 2340 2345 2350 2355 2360 2365 2370 2375 2380 2385 2390 2395 2400 2405 2410 2415 2420 2425 2430 2435 2440 2445 2450 2455 2460 2465 2470 2475 2480 2485 2490 2495 2500 2505 2510 2515 2520 2525 2530 2535 2540 2545 2550 2555 2560 2565 2570 2575 2580 2585 2590 2595 2600 2605 2610 2615 2620 2625 2630 2635 2640 2645 2650 2655 2660 2665 2670 2675 2680 2685 2690 2695 2700 2705 2710 2715 2720 2725 2730 2735 2740 2745 2750 2755 2760 2765 2770 2775 2780 2785 2790 2795 2800 2805 2810 2815 2820 2825 2830 2835 2840 2845 2850 2855 2860 2865 2870 2875 2880 2885 2890 2895 2900 2905 2910 2915 2920 2925 2930 2935 2940 2945 2950 2955 2960 2965 2970 2975 2980 2985 2990 2995 3000 3005 3010 3015 3020 3025 3030 3035 3040 3045 3050 3055 3060 3065 3070 3075 3080 3085 3090 3095 3100 3105 3110 3115 3120 3125 3130 3135 3140 3145 3150 3155 3160 3165 3170 3175 3180 3185 3190 3195 3200 3205 3210 3215 3220 3225 3230 3235 3240 3245 3250 3255 3260 3265 3270 3275 3280 3285 3290 3295 3300 3305 3310 3315 3320 3325 3330 3335 3340 3345 3350 3355 3360 3365 3370 3375 3380 3385 3390 3395 3400 3405 3410 3415 3420 3425 3430 3435 3440 3445 3450 3455 3460 3465 3470 3475 3480 3485 3490 3495 3500 3505 3510 3515 3520 3525 3530 3535 3540 3545 3550 3555 3560 3565 3570 3575 3580 3585 3590 3595 3600 3605 3610 3615 3620 3625 3630 3635 3640 3645 3650 3655 3660 3665 3670 3675 3680 3685 3690 3695 3700 3705 3710 3715 3720 3725 3730 3735 3740 3745 3750 3755 3760 3765 3770 3775 3780 3785 3790 3795 3800 3805 3810 3815 3820 3825 3830 3835 3840 3845 3850 3855 3860 3865 3870 3875 3880 3885 3890 3895 3900 3905 3910 3915 3920 3925 3930 3935 3940 3945 3950 3955 3960 3965 3970 3975 3980 3985 3990 3995 4000 4005 4010 4015 4020 4025 4030 4035 4040 4045 4050 4055 4060 4065 4070 4075 4080 4085 4090 4095 4100 4105 4110 4115 4120 4125 4130 4135 4140 4145 4150 4155 4160 4165 4170 4175 4180 4185 4190 4195 4200 4205 4210 4215 4220 4225 4230 4235 4240 4245 4250 4255 4260 4265 4270 4275 4280 4285 4290 4295 4300 4305 4310 4315 4320 4325 4330 4335 4340 4345 4350 4355 4360 4365 4370 4375 4380 4385 4390 4395 4400 4405 4410 4415 4420 4425 4430 4435 4440 4445 4450 4455 4460 4465 4470 4475 4480 4485 4490 4495 4500 4505 4510 4515 4520 4525 4530 4535 4540 4545 4550 4555 4560 4565 4570 4575 4580 4585 4590 4595 4600 4605 4610 4615 4620 4625 4630 4635 4640 4645 4650 4655 4660 4665 4670 4675 4680 4685 4690 4695 4700 4705 4710 4715 4720 4725 4730 4735 4740 4745 4750 4755 4760 4765 4770 4775 4780 4785 4790 4795 4800 4805 4810 4815 4820 4825 4830 4835 4840 4845 4850 4855 4860 4865 4870 4875 4880 4885 4890 4895 4900 4905 4910 4915 4920 4925 4930 4935 4940 4945 4950 4955 4960 4965 4970 4975 4980 4985 4990 4995 5000 5005 5010 5015 5020 5025 5030 5035 5040 5045 5050 5055 5060 5065 5070 5075 5080 5085 5090 5095 5100 5105 5110 5115 5120 5125 5130 5135 5140 5145 5150 5155 5160 5165 5170 5175 5180 5185 5190 5195 5200 5205 5210 5215 5220 5225 5230 5235 5240 5245 5250 5255 5260 5265 5270 5275 5280 5285 5290 5295 5300 5305 5310 5315 5320 5325 5330 5335 5340 5345 5350 5355 5360 5365 5370 5375 5380 5385 5390 5395 5400 5405 5410 5415 5420 5425 5430 5435 5440 5445 5450 5455 5460 5465 5470 5475 5480 5485 5490 5495 5500 5505 5510 5515 5520 5525 5530 5535 5540 5545 5550 5555 5560 5565 5570 5575 5580 5585 5590 5595 5600 5605 5610 5615 5620 5625 5630 5635 5640 5645 5650 5655 5660 5665 5670 5675 5680 5685 5690 5695 5700 5705 5710 5715 5720 5725 5730 5735 5740 5745 5750 5755 5760 5765 5770 5775 5780 5785 5790 5795 5800 5805 5810 5815 5820 5825 5830 5835 5840 5845 5850 5855 5860 5865 5870 5875 5880 5885 5890 5895 5900 5905 5910 5915 5920 5925 5930 5935 5940 5945 5950 5955 5960 5965 5970 5975 5980 5985 5990 5995 6000 6005 6010 6015 6020 6025 6030 6035 6040 6045 6050 6055 6060 6065 6070 6075 6080 6085 6090 6095 6100 6105 6110 6115 6120 6125 6130 6135 6140 6145 6150 6155 6160 6165 6170 6175 6180 6185 6190 6195 6200 6205 6210 6215 6220 6225 6230 6235 6240 6245 6250 6255 6260 6265 6270 6275 6280 6285 6290 6295 6300 6305 6310 6315 6320 6325 6330 6335 6340 6345 6350 6355 6360 6365 6370 6375 6380 6385 6390 6395 6400 6405 6410 6415 6420 6425 6430 6435 6440 6445 6450 6455 6460 6465 6470 6475 6480 6485 6490 6495 6500 6505 6510 6515 6520 6525 6530 6535 6540 6545 6550 6555 6560 6565 6570 6575 6580 6585 6590 6595 6600 6605 6610 6615 6620 6625 6630 6635 6640 6645 6650 6655 6660 6665 6670 6675 6680 6685 6690 6695 6700 6705 6710 6715 6720 6725 6730 6735 6740 6745 6750 6755 6760 6765 6770 6775 6780 6785 6790 6795 6800 6805 6810 6815 6820 6825 6830 6835 6840 6845 6850 6855 6860 6865 6870 6875 6880 6885 6890 6895 6900 6905 6910 6915 6920 6925 6930 6935 6940 6945 6950 6955 6960 6965 6970 6975 6980 6985 6990 6995 7000 7005 7010 7015 7020 7025 7030 7035 7040 7045 7050 7055 7060 7065 7070 7075 7080 7085 7090 7095 7100 7105 7110 7115 7120 7125 7130 7135 7140 7145 7150 7155 7160 7165 7170 7175 7180 7185 7190 7195 7200 7205 7210 7215 7220 7225 7230 7235 7240 7245 7250 7255 7260 7265 7270 7275 7280 7285 7290 7295 7300 7305 7310 7315 7320 7325 7330 7335 7340 7345 7350 7355 7360 7365 7370 7375 7380 7385 7390 7395 7400 7405 7410 7415 7420 7425 7430 7435 7440 7445 7450 7455 7460 7465 7470 7475 7480 7485 7490 7495 7500 7505 7510 7515 7520 7525 7530 7535 7540 7545 7550 7555 7560 7565 7570 7575 7580 7585 7590 7595 7600 7605 7610 7615 7620 7625 7630 7635 7640 7645 7650 7655 7660 7665 7670 7675 7680 7685 7690 7695 7700 7705 7710 7715 7720 7725 7730 7735 7740 7745 7750 7755 7760 7765 7770 7775 7780 7785 7790 7795 7800 7805 7810 7815 7820 7825 7830 7835 7840 7845 7850 7855 7860 7865 7870 7875 7880 7885 7890 7895 7900 7905 7910 7915 7920 7925 7930 7935 7940 7945 7950 7955 7960 7965 7970 7975 7980 7985 7990 7995 8000 8005 8010 8015 8020 8025 8030 8035 8040 8045 8050 8055 8060 8065 8070 8075 8080 8085 8090 8095 8100 8105 8110 8115 8120 8125 8130 8135 8140 8145 8150 8155 8160 8165 8170 8175 8180 8185 8190 8195 8200 8205 8210 8215 8220 8225 8230 8235 8240 8245 8250 8255 8260 8265 8270 8275 8280 8285 8290 8295 8300 8305 8310 8315 8320 8325 8330 8335 8340 8345 8350 8355 8360 8365 8370 8375 8380 8385 8390 8395 8400 8405 8410 8415 8420 8425 8430 8435 8440 8445 8450 8455 8460 8465 8470 8475 8480 8485 8490 8495 8500 8505 8510 8515 8520 8525 8530 8535 8540 8545 8550 8555 8560 8565 8570 8575 8580 8585 8590 8595 8600 8605 8610 8615 8620 8625 8630 8635 8640 8645 8650 8655 8660 8665 8670 8675 8680 8685 8690 8695 8700 8705 8710 8715 8720 8725 8730 8735 8740 8745 8750 8755 8760 8765 8770 8775 8780 8785 8790 8795 8800 8805 8810 8815 8820 8825 8830 8835 8840 8845 8850 8855 8860 8865 8870 8875 8880 8885 8890 8895 8900 8905 8910 8915 8920 8925 8930 8935 8940 8945 8950 8955 8960 8965 8970 8975 8980 8985 8990 8995 9000 9005 9010 9015 9020 9025 9030 9035 9040 9045 9050 9055 9060 9065 9070 9075 9080 9085 9090 9095 9100 9105 9110 9115 9120 9125 9130 9135 9140 9145 9150 9155 9160 9165 9170 9175 9180 9185 9190 9195 9200 9205 9210 9215 9220 9225 9230 9235 9240 9245 9250 9255 9260 9265 9270 9275 9280 9285 9290 9295 9300 9305 9310 9315 9320 9325 9330 9335 9340 9345 9350 9355 9360 9365 9370 9375 9380 9385 9390 9395 9400 9405 9410 9415 9420 9425 9430 9435 9440 9445 9450 9455 9460 9465 9470 9475 9480 9485 9490 9495 9500 9505 9510 9515 9520 9525 9530 9535 9540 9545 9550 9555 9560 9565 9570 9575 9580 9585 9590 9595 9600 9605 9610 9615 9620 9625 9630 9635 9640 9645 9650 9655 9660 9665 9670 9675 9680 9685 9690 9695 9700 9705 9710 9715 9720 9725 9730 9735 9740 9745 9750 9755 9760 9765 9770 9775 9780 9785 9790 9795 9800 9805 9810 9815 9820 9825 9830 9835 9840 9845 9850 9855 9860 9865 9870 9875 9880 9885 9890 9895 9900 9905 9910 9915 9920 9925 9930 9935 9940 9945 9950 9955 9960 9965 9970 9975 9980 9985 9990 9995 9999

isolation of said poly(ortho ester) at a temperature in the range of from 70 to 100 °C.

17. Coating compositions, comprising at least a binder component and a liquid carrier, wherein the binder is derived from one or more adducts according to claims 11-15, and optionally one or more additional comonomers, by copolymerization by means of a radical initiator, a cross-linker and a curing catalyst.

5 18. Coating compositions according to claim 17, characterized in that one of the additional components is formed by a hydroxyfunctional oligoether, derived from at least one polyol, free of carboxyl groups and having three or four hydroxyl groups and a monoglycidylester of an α,α -branched carboxylic acid containing from 5 to 10 15 carbon atoms.

15 19. Coating compositions according to claim 18, characterized in that the hydroxyfunctional oligoether applied, has a number average molecular weight M_n of from 150 to 1000, a molecular weight distribution $MWD < 1.10$ 20 and a hydroxy value of between 180 and 700.

20. Cured coating composition of claims 17-19 applied on a carrier or support.

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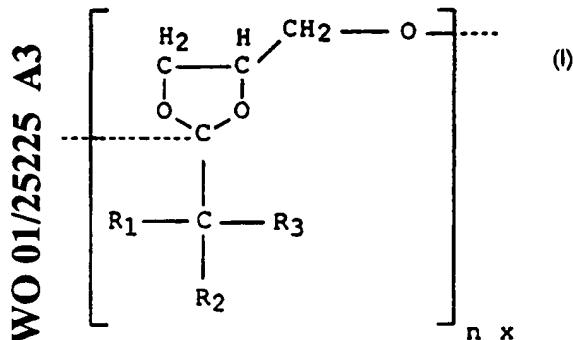
(71) Applicant (for all designated States except US): SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V. [NL/NL]; Carel van Bylandlaan 30, NL-2596 HR The Hague (NL).

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(54) Title: ADDUCTS OF GLYCIDYLESTERS OF ALPHA, ALPHA-BRANCHED CARBOXYLIC ACIDS AND ACRYLIC ACIDS AND POLY(ORTHO ESTER) AS INTERMEDIATE FOR THEIR PREPARATION

(57) Abstract: Poly(ortho ester) intermediate of general formula (I) wherein R₁, R₂, and R₃ are the same or different and each may represent an alkyl group containing from 1 to 10 carbon atoms and preferably from 1 to 6, wherein n represents an integer in the range of from 1 to 20 and preferably from 1 to 10; process for their preparation: adducts of glycidylesters and carboxylic acids and preferably acrylic acids, derived from said ortho esters; coating compositions comprising a binder component derived from said adducts.

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According to International Patent Classification (IPC) or to both national classification and IPC			
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 7 C07D			
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched			
Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal, WPI Data, CHEM ABS Data, BEILSTEIN Data, PAU			
C. DOCUMENTS CONSIDERED TO BE RELEVANT			
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Date of the actual completion of the International search 24 April 2001		Date of mailing of the International search report 04/05/2001	
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016		Authorized officer Stellmach, J	

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